



(11) **EP 2 402 379 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
04.01.2012 Bulletin 2012/01

(51) Int Cl.:
C08G 12/38 (2006.01) **C08G 12/12** (2006.01)
C08L 61/30 (2006.01) **C09J 161/30** (2006.01)

(21) Application number: **10168252.4**

(22) Date of filing: **02.07.2010**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO SE SI SK SM TR**
Designated Extension States:
BA ME RS

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(54) **Production method of urea-melamine-formaldehyde resin**

(57) The present invention relates to an environmentally sound method for the production of urea-melamine-formaldehyde resin characterized by the stagewise condensation of formaldehyde with urea and the subsequent co-condensation of the obtained prepolymer with melamine. Urea-formaldehyde concentrate may be used as formaldehyde feed for production of the urea-melamine-formaldehyde resin. The condensation with urea is performed in three stages by introducing urea batchwise. The process requires media with alternating acidity and heating supply. Deionized water may be used as viscos-

ity regulator. Borax may be introduced in the reaction mixture in the course of the co-condensation with melamine.

The obtained resin contains high concentrated dry residue, inconsiderable concentration of free formaldehyde and is stable during storage. It may be used as chemical hardeners e.g. for production of resin bonded and cellulose-fiber chipboards and other composite materials.

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Description

[0001] The present invention relates to chemical industry, in particular, production of synthetic resins (polymers) and directly concerns production of urea-melamine-formaldehyde resins which are widely used as manufacture hardeners for production of resin bonded and cellulose-fiber chipboards, composite materials, furniture and plywood adhesives as well as for production of various materials in construction industry and machinery manufacturing.

[0002] More specifically, the present invention relates to an environmentally sound method for the production of urea-melamine-formaldehyde resin characterized by the stagewise condensation of formaldehyde with urea and the subsequent condensation of the obtained prepolymer with melamine. Urea-formaldehyde concentrate may be used as formaldehyde feed for production of the urea-melamine-formaldehyde resin. The condensation with urea is performed in three stages by introducing urea batchwise. The process requires media with alternating acidity and heating supply. Deionized water may be used as viscosity regulator. Borax may be introduced in the reaction mixture in the course of the co-condensation with melamine.

[0003] The obtained resin contains high concentrated dry residue, inconsiderable concentration of free formaldehyde and is stable during storage. It may be used as chemical hardeners e.g. for production of resin bonded and cellulose-fiber chipboards and other composite materials.

[0004] All types of composite boards that have been prepared with urea-formaldehyde resins can be made with the resin of the present invention. Composite boards include, but are not limited to, particle boards and medium density fiber boards (MDF). The urea-melamine-formaldehyde resin of the present invention can be used as an adhesive in both the core and the face regions of the composite board.

[0005] Urea resin production based on use of urea-formaldehyde condensate is a well known method which is applied, for example, for gluing paper, wood and carton. This production method includes the following: preliminarily prepared condensation solution with urea : formaldehyde mol ratio 1-1.8:2.3 is mixed up with an additional amount of urea initially with pH=6-10 and then with pH=5.0 and is heated up to 90°C during 2-5 hours until the final urea : formaldehyde mol ratio equal to 1:0.4-1.4 is reached. This stage is followed by evaporation and cooling of the reaction product (GB 1480787, 1977).

[0006] Urea-formaldehyde resin produced as described above does not provide products on its basis with sufficiently high physical and mechanical properties since it has low adhesiveness and poor technological properties, besides it is toxic.

[0007] There is also another well known commercialized industrial multistage method of urea resins production in media with alternating acidity implying production of condensate solution on the first reaction stage by mixing urea aqueous solution with formaldehyde aqueous solution neutralized with sodium hydrate (to pH 7.0-8.65) with urea : formaldehyde mol ratio about 1.0:2.0; heating the made-up solution up to 80-100°C during 30-60 minutes; condensing the reaction mixture in acidic medium with pH 4-5 during 30-60 minutes at 90-100°C, then subsequently neutralizing the condensation product to pH 7.0-8.0, vacuum drying at 70-80°C and the final condensation with additional amount of urea in neutral or earthy base medium at 60-70°C during 30-60 minutes until the required total urea : formaldehyde mol ratio 1:1.0-2.0 in resin is obtained. (Re.: A.Ye. Anokhin and others. Wood industry. 1992, No.2, pages 12-16).

[0008] Produced by known methods resins have modest gluing and technological properties due to low contents of dry residues, unsatisfactory characteristics of stability, adhesion and miscibility with water and high toxicity due to free formaldehyde liberation which prevent to reach quality standards of cellulose-fiber chipboards higher than 2 class (according to GOST 10632 89).

[0009] There is also a proven technology for production of adhesives for glass fiber plastics which is based on modified melamine-formaldehyde resin obtained through condensation of melamine, formaldehyde and modifying ethylene glycol monoethyl ether at 80-85°C with pH 9-9.5 when melamine : formaldehyde mol ratio is 1:2.4 and monoethyl ether : melamine weight ratio is equal to 0.001:0.1-1 respectively (SU 729205, 1980).

[0010] This adhesive has high toxicity and rather modest characteristics of stability and miscibility with water. Such properties impede its use in wood industry, in particular for manufacturing chipboards.

[0011] In terms of technical resemblance to the claimed invention the following method of urea-formaldehyde resin production is most similar to it: It is based on urea containing condensation solution subject to subsequent condensation by heating in alkali medium on the first stage; on the second stage it is condensed by heating in weak acid medium until the required viscosity is obtained and its further condensation continues with additional amount of urea; on the third stage the condensation of the reaction product is completed by heating in alkali medium with subsequent cooling. In the condensation process mono- or polybasic alcohols are added in the product (SU 763368, 1980).

[0012] The first stage of the process is performed with pH 8.85-9.1 and 96-98°C, the second stage - with pH 5.0-5.3, while urea : formaldehyde mol ratio is 1:(1.9-2.0); then the product is cooled and the third stage is performed by condensing the product with an additional amount of urea until the final urea : formaldehyde mol ratio is reached, i.e. 1:1.40-1.45 with pH 7.5-8.3. Stabilizing alcohols are added in the amount of 8-25% of urea weight.

[0013] Resin produced as described above has E2 toxicity class if used for chipboards and simulated wood-veneer.

It prevents their use for manufacturing low toxic wood composition materials. The dry residue concentration in the resin is maximum 55.5% mass, free formaldehyde concentration makes 0.3-0.4% mass, the storage duration is 3-4 months, miscibility in water is 1-2. Addition of mono- or polybasic alcohols in condensation is a well-known method. For example, the mixture of guanamine with mono- and polybasic alcohol, alcohol amine and/or amine with their mol ratio 0,05 0,35 0,1 0,02 0,1a is used for producing melamine-formaldehyde oligomer and the above mixture is added during alkali condensation before melamine is added in the reaction medium (SU 1028696, 1983).

[0014] Water miscibility factor of the produced oligomers does not exceed 1-2.5, free formaldehyde concentration is 0.38-0.58% and their storage stability is maximum 30 days.

[0015] RU 2080334, 27.05.1997 depicts another method of urea-formaldehyde resin production which is as follows: urea containing condensation solution is first subject to condensation by heating in alkali medium; condensation by heating in weak acid medium on the second stage is performed until the required viscosity is obtained; on the third stage the solution is further condensed with an additional amount of urea in alkali medium with subsequent cooling of the reaction product; then mono- or polybasic alcohols are added in the course of condensation; the condensation solution is prepared by mixing urea containing feed and formaldehyde aqueous solution until urea : formaldehyde mol ratio becomes equal to 1.0:17-22; the final condensation with an additional amount of urea containing feed is performed with urea : formaldehyde mol ratio=1.0:0.95-1.3, and mono- or polybasic alcohols are added prior the final condensation in the amount of 0.01-0.2% of monomers weight.

[0016] Mono- or polybasic alcohols may be chosen from the following group: butanol, ethylene alcohol, glycerine, diethylene glycol, polyethyleneglycol, and pentaerythritol.

[0017] The first stage of the condensation reaction is performed with pH 6.5-9.0 at 80-90°C during 30-60 minutes and urea or urea-formaldehyde condensate are used as urea containing feed.

[0018] Urea-formaldehyde condensate is produced by mixing up urea excess with formaldehyde aqueous solution with pH 8.2-8.8 in the presence of an alkali agent with urea : formaldehyde mol ratio 0,8 2,0 1,0; the condensation of the prepared solution is performed at 5-45°C in the presence of alkali agent and it is followed with minimum three hour ageing of the obtained product.

[0019] The following matters can be used as an alkali agent: aqueous solutions of alkali metals hydroxides, amino compounds or their mixtures.

[0020] The process second stage is performed with pH 3.9-5.0 and 80-96°C until the required viscosity is obtained; after that (if necessary) the obtained reaction mixture is cooled down to 60-85°C and dried in vacuum.

[0021] The following matters can be used as an acid agent: benzene sulphonic acid, sulfuric acid, and ammonium chloride solution.

[0022] The third stage is performed upon completion of the vacuum drying at 40-65°C and with pH 7.0-8.5 during 25-60 minutes, and urea containing feed is added in the amount providing urea : formaldehyde mol ratio= 1:0.95-1.3.

[0023] The resin produced as described has lower toxicity and higher storage stability; free formaldehyde and dry residue concentration in product resin is maximum 0.11% and 64.7% respectively.

[0024] There are other methods of modified urea-formaldehyde resins production based on urea and formaldehyde polymerization by heating in media with alternating acidity and use of catalysts and modifiers allowing in some cases to produce resins with better properties. Various organic amines including polyethylenepolyamines are used as modifiers (RF Patent 2081886, 1997).

[0025] There is also a well-known method of modified urea-formaldehyde resin production based on urea and formaldehyde condensation first in alkali medium and afterwards in acidic medium in the presence of 0.0007-0.035 mol polyethylenepolyamines (PEPA) per 1 mol urea with the total urea and formaldehyde mol ratio 1:1.1-2.2 accordingly (USSR Certificate of Authorship No.1735312, 1992).

[0026] The fault of the final product resin produced as described above is high toxicity of the product and wood composition materials manufactured on its base corresponding to E2 toxic emission class. Apart from that the use of this modifier is limited with its high price and deficiency for resins production and therefore it cannot be applied as a constituent for production of a depressor agent in flotation process.

[0027] Reduction of urea-formaldehyde resins toxicity and their production cost is provided with the production method implying use of chloride sodium which being a waste product of polyethylenepolyamines production is applied as a PEPA containing modifier for urea and formaldehyde condensation (RF Patent 2078092, 1997).

[0028] The resin produced by using the above waste product as a modifier is not so expensive and in addition maintaining high main characteristics of the resin it has considerably lower concentration of free formaldehyde; however its properties are not in conformity with best resin standards.

[0029] RU 2249016, 27.11.2004 depicts another method of urea-formaldehyde resin production. Urea and formaldehyde condensation is performed with the initial urea and formaldehyde mol ratio=1:2.0-2.2 through several stages by heating in a medium with alternating acidity in the presence of polyvinyl alcohol aqueous solution used as a modifier. Urea-formaldehyde concentrate is used for condensation with urea as formaldehyde feed. The condensate contains 54-60%mass formaldehyde, 20-24 %mass urea, and the balance is water. The process is performed in the presence

of demineralized water adjusting viscosity and 1-3 weight parts of the modifier per 100 weight parts of urea. First the reaction mixture is heated up to $90 \pm 2^\circ\text{C}$ with pH 7.5-8.5, then it is kept under those conditions during 20 minutes, after that the temperature is decreased to $82-85^\circ\text{C}$ and with pH 4.5-5.0 the reaction mixture is aged during 20-50 minutes, then it is neutralized to pH 7.5-8.0 and an additional amount of urea is added to obtain the urea and formaldehyde mol ratio=1:1.5 and the mixture is aged during 60 minutes at $65-70^\circ\text{C}$. This method allows excluding waste water formation and increasing the process equipment capacity.

[0030] However the resin produced in the above described way still contains much free formaldehyde (0.11-0.20% mass.) which limits its application. This resin is mainly used for cellular plastic production.

[0031] All the methods described above are not applicable in the production of modified urea-formaldehyde resins such as urea-melamine-formaldehyde resins.

[0032] In addition, some prior art methods imply resin vacuum processing which causes formation of waste water containing formaldehyde and besides performing this stage takes some time and consumes energy.

[0033] The technical task of the claimed invention is simplification of the process, waste water reduction, improvement of environmental aspect and energy consumption at the expense of excluding the stage of concentrating the reaction mixture in vacuum. Urea-melamine-formaldehyde resins produced in claimed mode have low concentration of formaldehyde and provide the manufactured on their basis products with high physical and chemical characteristics.

[0034] The targeted technical task is solved by producing urea-melamine-formaldehyde resin by stagewise condensation of urea with formaldehyde which is followed with co-condensation of the produced prepolymer co-condensate with melamine by heating in media with alternating acidity. After the co-condensation stage with melamine the final condensation of the reaction product with urea is performed whereas urea-formaldehyde concentrate is preferably used as formaldehyde feed. When condensing formaldehyde (such as urea-formaldehyde condensate or urea-formaldehyde concentrate) with urea the latter is introduced batchwise in three stages; the initial stage of the condensation is preferably conducted in the presence of deionized water regulating viscosity and the stage of co-condensation with melamine is preferably performed in the presence of borax, meanwhile the final condensation stage preferably continues until urea : melamine : formaldehyde mol ratio is 1 : 0.07 : 1.2.

[0035] Besides if necessary a modifier is additionally introduced in the reaction mixture on the stage of the final condensation of the reaction product with urea preferably in the amount of 0.5-5.0% mass. of the total urea added. Said modifier is preferably chosen from the following group: mono- or polybasic alcohols, starch, polyvinyl alcohol, and polysiloxane liquid.

[0036] As formaldehyde feed urea-formaldehyde concentrate aqueous solution with pH=6.5 - 8.5 with the following composition can be used (%mass.):

urea	20-24
formaldehyde	54-60
methanol	≤ 0.3 .

[0037] Thus the targeted task is solved by using urea-formaldehyde concentrate (UFC) as formaldehyde feed for condensing urea (U), melamine (M) and formaldehyde (F) by heating in the medium with alternating acidity. The process of resin formation is preferably performed in the presence of demineralized water adjusting viscosity by co-condensation with melamine preferably in alkali medium preferably in the presence of borax as buffer additive.

[0038] The gist of the solution suggested is a urea-melamine-formaldehyde synthesis that is preferably performed by condensing UFC with the 1st batch of urea, preferably with the added viscosity regulator, preferably with pH = 5.6 - 7.2, preferably at $20 - 40^\circ\text{C}$. Then the second batch of urea is loaded to reach preferably the F : U mol ratio = (2.3 - 1.98): 1.0; the mixture is heated up to preferably $90 - 92^\circ\text{C}$. Then the temperature is decreased to preferably $80 - 82^\circ\text{C}$; and to reach preferably pH= 4.5 - 5.5 H_2SO_4 2%-solution, e.g., is added and the acid polycondensation (and/or condensation) takes place. Further the reaction mixture is neutralized preferably with NaOH solution to obtain preferably pH=9.0 - 10.0. When the reaction mixture temperature is preferably $80 - 88^\circ\text{C}$, melamine and preferably borax are added in the amount of preferably 0.04 - 0.25 mols melamine per 1 mol urea.

[0039] The condensation is preferably performed with pH = 9,0 - 10,0 at preferably 80°C .

[0040] Then the obtained product is cooled to preferably 70°C , the third batch of urea and optionally further formaldehyde such as urea-formaldehyde concentrate (UFC) is added, thus reaching formaldehyde : urea mol ratio equal to preferably (1.1 - 1.2) : 1 respectively and then the final condensation is performed at preferably $65 - 70^\circ\text{C}$. Preferably, the reaction mixture is cooled and discharged.

[0041] Urea-formaldehyde concentrate UFC-80 or UFC-85, for example, can be used as formaldehyde feed with the following composition (%mass.): urea - 20 - 24%, formaldehyde - 54 - 60%, the balance is water; UFC may be produced by oxidative hydrogenation of methanol on iron-molybdenum catalyst in the tubular reactor with subsequent chemisorption of formaldehyde containing gas with urea solution.

[0042] NaOH and H₂SO₄ aqueous solutions may be used to regulate pH of the reaction mixture. Demineralized water is preferably used to adjust viscosity of the reaction mixture and borax (e.g sodium tetraborate decahydrate) or any other sodium polyborate is preferably applied as a buffer agent.

[0043] In addition a modifier may be introduced (added) in the reaction mixture on the stage of the final condensation of the reaction product with urea. One of the following matters may be chosen as a modifier from the following group: mono- or polybasic alcohols (for example, methanol, and pentaerythritol), starch, polyvinyl alcohol, and polysiloxane liquid and mixtures thereof.

In another embodiment, the present invention is directed to the following aspects:

[0044]

1. It includes the method of production of urea-melamine-formaldehyde resin by stagewise condensation of formaldehyde with urea and subsequent co-condensation of the obtained prepolymer with melamine by heating in media with alternating acidity. After the co-condensation with melamine the reaction product is subject to the final condensation with urea which *is characterized in that* its coming from urea-formaldehyde condensate used as formaldehyde feed. Urea is added batchwise in three stages during the condensation of urea-formaldehyde condensate with urea. The initial stage of the condensation is performed in the presence of deionized water adjusting viscosity. The co-condensation with melamine is performed in the presence of borax.

2. The method of production of urea-melamine-formaldehyde resin as per paragraph 1 is *characterized in that* on the stage of the reaction product final condensation a modifier - mono- or polybasic alcohols, starch, polyvinyl alcohol, or polysiloxane liquid - is additionally introduced into the reaction mixture in the amount of 0.5-5.0 %mass. of the total urea added.

Detailed description of the invention

[0045] The present invention relates to a method for the production of urea-melamine-formaldehyde resin, preferably with a urea : melamine : formaldehyde mol ratio of 1 : 0.07 : 1.2 without the need of concentrating the reaction mixture in vacuum. Inter alia due to the fact that the present invention allows for the omission of concentrating the reaction mixture in vacuum, the claimed method is environmentally sound.

[0046] The claimed method for the production of urea-melamine-formaldehyde resin is characterized by the stepwise performance of an urea-formaldehyde-condensation reaction before performing a co-condensation reaction with melamine, wherein said stepwise performance of an urea-formaldehyde-condensation reaction comprises (or consists of) the addition of urea to the reaction product or products of a first urea-formaldehyde-condensation reaction, and wherein said first urea-formaldehyde-condensation reaction is performed at a pH between 4.0 and 9.0, and at a temperature below 80°C and optionally in the presence of a viscosity regulator such as demineralized water. Said first urea-formaldehyde-condensation reaction comprises the addition of urea to a composition comprising formaldehyde (such as urea-formaldehyde concentrate (UFC)), preferably in an amount to reach a formaldehyde:urea mol ratio of from 1.5:1.0 to 6.0:1.0, more preferably in an amount to reach a formaldehyde:urea mol ratio of from 3.0:1.0 to 5.0:1.0 and most preferably of from 4.0:1.0 to 4.6:1.0. Preferably, none of the following components is used (i.e. added the reaction mixture) during the claimed method: phenol, ammonium nitrate, caprolactam, hexamine, monoethanolamine and/or triethanolamine. Accordingly, the claimed resin is preferably not the condensation product of formaldehyde, urea and phenol and is preferably not the condensation product of formaldehyde, urea, melamine and phenol.

[0047] Optionally, said first urea-formaldehyde-condensation reaction is performed at a pH between 5.0 and 8.0, preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2. Preferably, said first urea-formaldehyde-condensation reaction is performed in absence of monoethanolamine.

[0048] Optionally, said first urea-formaldehyde-condensation reaction is performed at a temperature below 70 °C, preferably below 60°C, more preferably below 50°C and most preferably between 20 and 40 °C.

[0049] Optionally, said co-condensation reaction with melamine is performed in the presence of a buffer additive such as borax, preferably in alkali medium, more preferably at pH 9.0 to 10.0.

[0050] Optionally, urea-formaldehyde concentrate (UFC), optionally as aqueous solution, is used as formaldehyde feed. The urea-formaldehyde concentrate (UFC) according to the present invention preferably comprises 20-24 %mass urea, 54-60 %mass formaldehyde and up to 0.3 %mass methanol and has preferably a pH of 6.5 to 8.5. Optionally, at least one modifier or additive such as polysiloxane liquid, starch, polyvinyl alcohol, mono- or polybasic alcohols (such as butanol, ethylene alcohol, glycerine, diethylene glycol, polyethyleneglycol, methanol and/or pentaerythritol), or mixtures thereof, is added to the reaction product or products of said co-condensation reaction with melamine, wherein the amount of said modifiers is preferably in the range from 0.5 to 5.0 %mass of the total urea added, more preferably in

the range from 1.5 to 4.0 %mass of the total urea added.

[0051] Generally, a condensation reaction is a chemical reaction in which two molecules or moieties (functional groups) combine to form one single molecule, together with the loss of a small molecule. Said small molecule may be water. Methylolureas, for example, may react with a -NHR moiety (R may be H or any other residue) of urea or of a derivative of urea. Methylolureas are possible (intermediate) products in a urea-formaldehyde-condensation and are typically the products of an addition reaction between formaldehyde and urea or between formaldehyde and a derivative of urea. Said methylolureas include mono(hydroxymethyl)urea and poly(hydroxymethyl)urea such as di(hydroxymethyl)urea.

[0052] A series of condensation steps may take place whereby monomers or monomer chains add to each other to form longer chains. This is sometimes termed 'condensation polymerization' or 'step-growth polymerization'. Urea-formaldehyde-condensation reactions may or may not be such condensation polymerizations.

[0053] In the context of the present invention, urea-formaldehyde-condensations (such as said first and second urea-formaldehyde-condensation) are chemical reactions whose educts comprise or consist of urea, formaldehyde and optionally also methylolureas (i.e. this definition does not exclude the presence of intermediate products such as mono(hydroxymethyl)urea and poly(hydroxymethyl)urea) and optionally a viscosity regulator and/or a solvent such as water and/or methanol. Typically, a reaction mixture comprising urea and formaldehyde is heated when performing a urea-formaldehyde-condensation. As formaldehyde feed, urea-formaldehyde concentrate (UFC) may be used. The course of a urea-formaldehyde-condensation reaction is mainly determined by the amounts of the educts, by the reaction temperature and by the pH of the reaction mixture.

[0054] In the context of the present invention, the terms "*co-condensation with melamine*" and "*co-condensation reaction with melamine*" are used synonymously and stand for chemical reactions whose educts comprise or consist of melamine, the reaction product or products of a urea-formaldehyde-condensation according to the present invention and optionally borax and/or a solvent. According to the present invention, the co-condensation with melamine is preferably performed in the presence of a polyborate salt, preferably in alkali medium. Said polyborate salt is preferably a sodium polyborate such as borax (e.g. sodium tetraborate decahydrate).

[0055] The present invention is also directed to the use of demineralized or deionized water as viscosity regulator during the production of a urea-melamine-formaldehyde resin, in particular during said first and/or second urea-formaldehyde-condensation. In the context of the present invention, the terms "*demineralized water*" and "*deionized water*" are used synonymously.

[0056] Generally, an acidic reaction medium may be neutralized with any appropriate alkaline neutralizing agent known in the art, such as an alkali metal hydroxide, alkali metal carbonates, alkaline earth hydroxides, organic amines, or mixtures thereof. Preferably, NaOH is used. Similarly, an alkali reaction medium may be neutralized with any appropriate acidic neutralizing agent known in the art, such as H₂SO₄ (=sulfuric acid), benzene sulphonic acid, and ammonium chloride solution.

[0057] In a preferred embodiment, the method according to the present invention comprises the following steps or consists of the following steps:

(a) providing a composition comprising formaldehyde, preferably at a pH of 6.5-8.5, such as providing a urea-formaldehyde concentrate (UFC);

(b) providing an amount of urea to reach an formaldehyde:urea mol ratio of from 1.5:1.0 to 2.5:1.0, preferably of from 1.98:1.0 to 2.3:1.0, and dividing said amount of urea into two equal batches of urea and thus providing a first and a second batch of urea; adding one of said two batches of urea to said composition comprising formaldehyde;

(c) optionally adding a viscosity regulator to the mixture, such as demineralised or deionized water;

(d) agitating the mixture, preferably until complete dissolution of the added batch of urea, at a temperature less than 70 °C, preferably less than 60 °C, more preferably less than 50°C and most preferably at a temperature between 20 and 40 °C, and, if necessary, adjusting the pH to a value between 4.0 and 9.0, preferably between 5.0 and 8.0, more preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2; it is believed that a first urea-formaldehyde-condensation reaction is performed during step (b), (c) and/or (d)

(e) adding the second batch of urea, and subsequently heating the mixture under agitation, preferably to 80-100 °C, more preferably to 90-92 °C; then aging the mixture preferably for at least 10-15 minutes. Preferably no ammonium nitrate is added before, during and/or after said aging.

(f) adjusting the temperature of the mixture, preferably to 75-85 °C, more preferably to 80-82 °C and adjusting the pH of the mixture, preferably to 3.0-5.5, more preferably to 4.5-5.5, preferably with a 2-% H₂SO₄ solution. Preferably, the reaction is continued until the addition of 1-10 drops of the reaction mixture to 10-1000 ml cold water causes

stable turbidness. The most widely used measurement unit for turbidity is the FTU (Formazin Turbidity Unit), also referred to as Nephelometric Turbidity Unit (NTU). "Stable turbidness" means that the NTU is at least 100 and does not significantly change over time. It is believed that a second urea-formaldehyde-condensation reaction, i.e. an acid condensation, is performed during steps (e) and/or (f).

(g) raising the pH of the mixture to obtain an alkali medium, preferably raising the pH of the mixture to 9.0-10.0, preferably with a NaOH solution;

(h) adding melamine and optionally adding at least one additive (e.g. a buffer additive) such as borax to the reaction mixture for performing a co-condensation reaction with melamine, preferably at the temperature of 70-90 °C, more preferably at a temperature of 80-88 °C, the amount of melamine being preferably in the range of 0.02 to 0.4 mol melamine per 1 mol urea, being more preferably in the range of 0.04 to 0.25 mol melamine per 1 mol urea; continuing said reaction, preferably at pH 9.0-10.0 and/or preferably at the temperature of 80 °C and/or preferably for 20-30 minutes. Said additive is preferably a polyborate salt and more preferably a sodium polyborate such as borax (e.g. sodium tetraborate decahydrate).

(i) adjusting the temperature of the reaction mixture, preferably to a temperature of 50 to 80 °C, more preferably to a temperature of 60 to 70 °C;

(j) adding a third batch of urea and optionally adding formaldehyde (preferably in the form of urea-formaldehyde concentrate (UFC)) to the reaction mixture, preferably to reach a formaldehyde:urea mol ratio in the range of 1.1:1 to 1.2:1, more preferably to reach a formaldehyde:urea:melamine mol ratio of 1.2:1:0.07.

[0058] Preferably, said urea-formaldehyde concentrate (UFC) comprises 20-24 %mass urea, 54-60 %mass formaldehyde and up to 0.3 %mass methanol and has preferably a pH of 6.5 to 8.5;

(k) optionally adding at least one modifier or additive such as polysiloxane liquid, starch, polyvinyl alcohol, mono- or polybasic alcohols, such as methanol and pentaerythritol, or mixtures thereof, preferably in an amount of 0.5 to 5.0 %mass of the total urea added, more preferably in an amount of 1.5 to 4.0 %mass of the total urea added;

(1) agitating the reaction mixture, preferably at a temperature between 55 and 75 °C, more preferably at a temperature between 65 and 70 °C and preferably at a pH of 7.0 to 9.5, more preferably at a pH of 8.0 to 8.5, and preferably for at least 30-35 minutes and then cooling the reaction mixture to 25-30 °C, preferably to room temperature; it is believed that a further, final condensation reaction is performed during step (j), (k) and/or (1).

[0059] The present invention is also directed to urea-melamine-formaldehyde resin obtainable according to the above outlined steps (a) to (1). Preferably, the urea-melamine-formaldehyde resin according to the present invention has a formaldehyde:urea:melamine mol ratio between 1.0:1:0.07 and 1.4:1:0.07 or between 1.2:1:0.04 and 1.2:1:0.25. More preferably the formaldehyde:urea:melamine mol ratio is in the range (1.0 to 1.2):1:(0.04 to 0.25), wherein the amount of formaldehyde and melamine are selected independently from each other. Most preferably, the formaldehyde:urea:melamine mol ratio is 1.2:1:0.07

[0060] The present invention is also directed to the use of the urea-melamine-formaldehyde resin according to the present invention as adhesive, e.g. as furniture adhesive or as plywood adhesive. Said adhesive is preferably used for gluing paper, wood, carton or mixtures thereof. Accordingly, the urea-melamine-formaldehyde resin according to the present invention can be used for the production of composite materials such as resin bonded and cellulose-fibre chipboards and other materials used in construction industry and machinery manufacturing.

[0061] The present invention is also directed composite materials comprising the urea-melamine-formaldehyde resin according to the present invention, such as composite boards, bonded and cellulose-fibre chipboards, particle boards and medium density fiber boards (MDF).

[0062] The present invention is also directed to a composition that can be used in the production of urea-melamine-formaldehyde resins. Said composition is obtainable by a method comprising the steps or consisting of the steps:

(a) providing a composition comprising formaldehyde, preferably at a pH of 6.5-8.5, such as providing a urea-formaldehyde concentrate (UFC);

(b) providing an amount of urea to reach an formaldehyde:urea mol ratio of 1.5:1.0 to 2.5:1.0, preferably of 1.98:1.0 to 2.3:1.0, and dividing said amount of urea into two equal batches of urea and thus providing a first and a second batch of urea; adding one of said two batches of urea to said composition comprising formaldehyde;

(c) optionally adding a viscosity regulator to the mixture, such as demineralised or deionized water;

(d) agitating the mixture, preferably until complete dissolution of the added batch of urea, at a temperature less than 70 °C, preferably less than 60 °C, more preferably less than 50°C and most preferably at a temperature between 20 and 40 °C, and, if necessary, adjusting the pH to a value between 4.0 and 9.0, preferably between 5.0 and 8.0, more preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2;

(e) adding the second batch of urea, and subsequently heating the mixture under agitation, preferably to 80-100 °C, more preferably to 90-92 °C; then aging the mixture, preferably for at least 10-15 minutes. Preferably no ammonium nitrate is added before, during and/or after said aging.

[0063] Preferably, none of the following components is used (i.e. added the reaction mixture) when producing said composition that can be used in the production of urea-melamine-formaldehyde resins: ammonium nitrate, caprolactam, hexamine, monoethanolamine and/or triethanolamine.

[0064] Skilled practitioners recognize that the reactants are commercially available in many forms. Any form which can react with the other reactants and which does not introduce extraneous moieties deleterious to the desired reaction and reaction product can also be used in the claimed methods, such as in the preparation of the urea-melamine-formaldehyde resin of the present invention.

[0065] Formaldehyde is available in many forms. Paraform (solid, polymerized formaldehyde) and formalin solutions (aqueous solutions of formaldehyde, sometimes with methanol, in 37 percent, 44 percent, or 50 percent formaldehyde concentrations) are commonly used forms. Formaldehyde also is available as a gas. Any of these forms is suitable for use in the practice of the invention. Typically, formalin solutions are preferred as the formaldehyde source.

[0066] Similarly, urea is available in many forms. Solid urea, such as prill, and urea solutions, typically aqueous solutions, are commonly available. Further, urea may be combined with another monomer, most typically formaldehyde and urea-formaldehyde, often in aqueous solution. Any form of urea or urea in combination with formaldehyde is suitable for use in the practice of the invention. Both urea prill and combined urea-formaldehyde products are preferred, such as Urea Formaldehyde Concentrate or UFC 85.

[0067] Although melamine is specifically mentioned, in the practice of this invention, the melamine may be totally or partially replaced with other aminotriazine compounds. Other suitable aminotriazine compounds include substituted melamines, or cycloaliphatic guanamines, or mixtures thereof. Substituted melamines include the alkyl melamines and aryl melamines which can be mono-, di-, or tri-substituted. In the alkyl substituted melamines, each alkyl group can contain 1-6 carbon atoms and, preferably 1-4 carbon atoms. Typical examples of some of the alkyl-substituted melamines are monomethyl melamine, dimethyl melamine, trimethyl melamine, monoethyl melamine, and 1-methyl-3-propyl-5-butyl melamine. In the aryl-substituted melamines, each aryl group can contain 1-2 phenyl radicals and, preferably, 1 phenyl radical. Typical examples of an aryl-substituted melamine are monophenyl melamine and diphenyl melamine.

[0068] The below examples can illustrate the claimed invention, however, do not limit its possible application.

Example No. 1

[0069] A reactor furnished with an agitator, a backflow condenser, and a thermometer is loaded with UFC, demineralized water and urea with formaldehyde : urea mol ratio = F : U = 1.98 : 1. Urea is divided into two batches (equal I and II). After the complete dilution of the first urea batch a pH-test of the reaction mixture is made, and pH value should be in the range 5.6 - 7.2. After that the second urea batch is loaded and the mixture under agitation is heated up to 90 - 92°C. Then the reaction mixture is aged.

[0070] Further the temperature of the reaction mixture is reduced to 80 - 82°C and, H₂SO₄ 2%-solution, for example, is added to obtain pH level of the reaction mixture equal to 4,5 - 5,5. Then the mixture is neutralized, for example, with NaOH 4%-solution to obtain pH level = 9.0 - 10.0, and afterwards borax and melamine are loaded. The condensation of the mixture is performed with pH 9.0 - 10.0 at 80°C. Then the reaction mixture temperature is decreased to 70°C. After that an additional amount of urea is introduced to reach formaldehyde : urea : melamine mol ratio = F : U : M = 1.2 : 1 : 0.07 and the condensation continues with pH = 8.0 - 8.5 at 65 - 70°C. Then the reaction mixture is cooled to 25 - 30°C and discharged.

Example No. 2

[0071] A reactor furnished with an agitator, a backflow condenser, and a thermometer is loaded with UFC, demineralized water and urea with formaldehyde : urea mol ratio = F : U = 2.1 : 1. Urea is divided into two batches (equal I and II). After the complete dilution of the first urea batch a pH-test of the reaction mixture is made, and pH value should be in the range 5.6 - 7.2. After that the second urea batch is loaded and the mixture under agitation is heated up to 90 - 92°C.

Then the reaction mixture is aged.

[0072] Further the temperature of the reaction mixture is reduced to 80 - 82°C and, H₂SO₄ 2%-solution, for example, is added to obtain pH level of the reaction mixture equal to 4,5 - 5,5. Then the mixture is neutralized, for example, with NaOH 4%-solution to obtain pH level = 9.0 - 10.0, and afterwards borax and melamine are loaded. The condensation of the mixture is performed with pH 9.0 - 10.0 at 80°C. Then the reaction mixture temperature is decreased to 70°C. After that an additional amount of urea is introduced to reach formaldehyde : urea : melamine mol ratio = F : U : M = 1.2 : 1 : 0.07 and the condensation continues with pH = 8.0 - 8.5 at 65 - 70°C. Then the reaction mixture is cooled to 25 - 30°C and discharged.

Example No.3

[0073] A reactor furnished with an agitator, a backflow condenser, and a thermometer is loaded with UFC, demineralized water and urea with formaldehyde : urea mol ratio = F : U = 2.3 : 1. Urea is divided into two batches (equal I and II). After the complete dilution of the first urea batch a pH-test of the reaction mixture is made, and pH value should be in the range 5.6 - 7.2. After that the second urea batch is loaded and the mixture under agitation is heated up to 90 - 92°C. Then the reaction mixture is aged.

[0074] Further the temperature of the reaction mixture is reduced to 80 - 82°C and, H₂SO₄ 2%-solution, for example, is added to obtain pH level of the reaction mixture equal to 4,5 - 5,5. Then the mixture is neutralized, for example, with NaOH 4%-solution to obtain pH level = 9.0 - 10.0, and afterwards borax and melamine are loaded. The condensation of the mixture is performed with pH 9.0 - 10.0 at 80°C. Then the reaction mixture temperature is decreased to 70°C. After that an additional amount of urea is introduced to reach formaldehyde : urea : melamine mol ratio = F : U : M = 1.2 : 1 : 0.07 and the condensation continues with pH = 8.0 - 8.5 at 65 - 70°C. Then the reaction mixture is cooled to 25 - 30°C and discharged.

[0075] The comparative characteristics of resins produced by the claimed method and traditional methods are presented in the Table.

Table

Properties of Treating Urea-Melamine-Formaldehyde Resins Produced by the Claimed Method and as per Prototype				
Properties	Values			
	Prototype	Examples		
		1	2	3
Formaldehyde:urea: melamine mol ratio	(1.0-1.3) :1: (0.04 - 0.25)	1.2: 1 : 0.07	1.2:1: 0.07	1.2:1 : 0.07
Mass fraction of dry residue, %	54-67,5	62	67	63
Mass fraction of free formaldehyde in resin, %	0.04-0.07	0.06	0.05	0.04
Hydrogen ion concentration, pH	7.7-8.7	7.7-8.7	7.7-8.7	7.7-8.7
Resin storage time, months	> 6	>6	>6	>6

[0076] Thus by applying the claimed method it is possible to produce high quality urea-melamine-formaldehyde resins excluding vacuuming stage and thus, the claimed method solves at least three problems, i.e.:

- improving environmental safety by excluding waste water formation;
- reducing energy consumption for resin synthesis; and
- improving the resin quality.

Claims

1. A method for the production of urea-melamine-formaldehyde resin, preferably with a urea : melamine : formaldehyde

mol ratio of 1 : 0.07 : 1.2 and preferably without the step of concentrating the reaction mixture in vacuum, **characterized by** the stepwise performance of an urea-formaldehyde-condensation reaction before performing a co-condensation reaction with melamine,

wherein said stepwise performance of an urea-formaldehyde-condensation reaction comprises the addition of urea to the reaction products of a first urea-formaldehyde-condensation reaction, and

wherein said first urea-formaldehyde-condensation reaction is performed at a pH between 4.0 and 9.0, and at a temperature below 80°C and optionally in the presence of a viscosity regulator such as demineralized water and comprises the addition of urea to a composition comprising formaldehyde, preferably in an amount to reach a formaldehyde:urea mol ratio of from 1.5:1.0 to 6.0:1.0.

2. The method according to claim 1, wherein said pH is between 5.4 and 8.0, preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2.

3. The method according to claim 1 or 2, wherein said temperature is below 70 °C, preferably below 60°C, more preferably below 50°C and most preferably between 20 and 40 °C.

4. The method according to anyone of claims 1 to 3, wherein said co-condensation reaction with melamine is performed in the presence of a polyborate salt such as borax, preferably in alkali medium, more preferably at pH 9.0 to 10.0.

5. The method according to anyone of claims 1 to 4, wherein at least one modifier or additive such as polysiloxane liquid, starch, polyvinyl alcohol, mono- or polybasic alcohols, such as methanol and pentaerythritol, or mixtures thereof, is added to the reaction product of said co-condensation reaction with melamine, wherein the amount of said modifiers is preferably in the range from 0.5 to 5.0 %mass of the total urea added, more preferably in the range from 1.5 to 4.0 %mass of the total urea added.

6. The method according to anyone of claims 1 to 5 comprising the steps:

(a) providing a composition comprising formaldehyde, preferably at a pH of 6.5-8.5, such as providing a urea-formaldehyde concentrate (UFC);

(b) providing an amount of urea to reach an formaldehyde:urea mol ratio of from 1.5:1.0 to 2.5:1.0, preferably of 1.98:1.0 to 2.3:1.0, and dividing said amount of urea into two equal batches of urea and thus providing a first and a second batch of urea; adding one of said two batches of urea to said composition comprising formaldehyde;

(c) optionally adding a viscosity regulator to the mixture, such as demineralised or deionized water;

(d) agitating the mixture, preferably until complete dissolution of the added batch of urea, at a temperature less than 70 °C, preferably less than 60 °C, more preferably less than 50°C and most preferably at a temperature between 20 and 40 °C, and, if necessary, adjusting the pH to a value between 4.0 and 9.0, preferably between 5.0 and 8.0, more preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2;

(e) adding the second batch of urea, and subsequently heating the mixture under agitation, preferably to 80-100 °C, more preferably to 90-92 °C; then aging the mixture, preferably for at least 10-15 minutes.

7. The method according to anyone of claim 1 to 6, wherein urea-formaldehyde concentrate (UFC), optionally as aqueous solution, is used as formaldehyde feed and wherein said urea-formaldehyde concentrate (UFC) preferably comprises 20-24 %mass urea, 54-60 %mass formaldehyde and up to 0.3 %mass methanol and has preferably a pH of 6.5 to 8.5.

8. The method according to claim 6 or 7, followed by the step comprising:

(f) adjusting the temperature of the mixture, preferably to 75-85 °C, more preferably to 80-82 °C and adjusting the pH of the mixture, preferably to 3.0-5.5, more preferably to 4.5-5.5, preferably with a 2-% H₂SO₄ solution; and preferably continuing the reaction until the addition of 1-10 drops of the reaction mixture to 10-1000 ml cold water causes stable turbidness.

9. The method according to claim 8, followed by the steps comprising:

(g) raising the pH of the mixture to obtain an alkali medium, preferably raising the pH of the mixture to 9.0-10.0, preferably with a NaOH solution;

(h) adding melamine and optionally adding at least one buffer additive such as borax to the reaction mixture for performing a co-condensation reaction with melamine, preferably at the temperature of 70-90 °C, more preferably at a temperature of 80-88 °C, the amount of melamine being preferably in the range of 0.02 to 0.4 mol melamine per 1 mol urea, being more preferably in the range of 0.04 to 0.25 mol melamine per 1 mol urea; continuing said reaction preferably at the temperature of 80°C and/ or preferably for 20-30 minutes.

10. The method according to claim 9, followed by the steps comprising:

(i) adjusting the temperature of the reaction mixture, preferably to a temperature of 50 to 80 °C, more preferably to a temperature of 60 to 70 °C;

(j) adding a third batch of urea and optionally adding formaldehyde, preferably urea-formaldehyde concentrate (UFC) according to claim 7, to the reaction mixture, preferably to reach a formaldehyde:urea mol ratio in the range of 1.1:1 to 1.2:1, more preferably to reach a formaldehyde:urea:melamine mol ratio of 1.2:1:0.07;

(k) optionally adding at least one modifier or additive such as polysiloxane liquid, starch, polyvinyl alcohol or mono- or polybasic alcohols, such as methanol and pentaerythritol, or mixtures thereof, preferably in an amount of 0.5 to 5.0 %mass of the total urea added, more preferably in an amount of 1.5 to 4.0 %mass of the total urea added;

(l) agitating the reaction mixture, preferably at a temperature between 55 and 75 °C, more preferably at a temperature between 65 and 70 °C and preferably at a pH of 7.0 to 9.5, more preferably at a pH of 8.0 to 8.5, preferably for at least 30-35 minutes and then cooling the reaction mixture to 25-30 °C, preferably to room temperature.

11. Urea-melamine-formaldehyde resin prepared according to anyone of claims 1 to 10; preferably in a formaldehyde:urea:melamine mol ratio between 1.1:1:0.07 and 1.3:1:0.07 or between 1.2:1:0.06 and 1.2:1:0.08, more preferably in a formaldehyde:urea:melamine mol ratio of 1.2:1:0.07.

12. Use of the resin according to claim 11 as adhesive such as furniture or plywood adhesive, preferably for gluing paper, wood, carton or mixtures thereof, in particular for the production of composite materials such as resin bonded and cellulose-fibre chipboards and other materials used in construction industry and machinery manufacturing.

13. Composite materials, such as composite boards, comprising the urea-melamine-formaldehyde resin of claim 11 and objects, comprising said composite materials.

14. Composition for preparing urea-melamine-formaldehyde resins, said composition being obtainable by a method comprising the steps or consisting of the steps:

(a) providing a composition comprising formaldehyde, preferably at a pH of 6.5-8.5, such as providing a urea-formaldehyde concentrate (UFC);

(b) providing an amount of urea to reach an formaldehyde:urea mol ratio of 1.5:1.0 to 2.5:1.0, preferably of 1.98:1.0 to 2.3:1.0, and dividing said amount of urea into two equal batches of urea and thus providing a first and a second batch of urea; adding one of said two batches of urea to said composition comprising formaldehyde;

(c) optionally adding a viscosity regulator to the mixture, such as demineralised or deionized water;

(d) agitating the mixture, preferably until complete dissolution of the added batch of urea, at a temperature less than 70 °C, preferably less than 60 °C, more preferably less than 50°C and most preferably at a temperature between 20 and 40 °C, and, if necessary, adjusting the pH to a value between 4.0 and 9.0, preferably between 5.0 and 8.0, more preferably between 5.2 and 7.6, and most preferably between 5.6 and 7.2;

(e) adding the second batch of urea, and subsequently heating the mixture under agitation, preferably to 80-100 °C, more preferably to 90-92 °C; then aging the mixture, preferably for at least 10-15 minutes.

15. Use of demineralized or deionized water as viscosity regulator during the production of a urea-melamine-formaldehyde resin such as use of demineralized or deionized water as viscosity regulator during a urea-formaldehyde-condensation.



EUROPEAN SEARCH REPORT

Application Number
EP 10 16 8252

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